Electrochemistry

CHE 3053

Kinetics of Electrochemical Reactions

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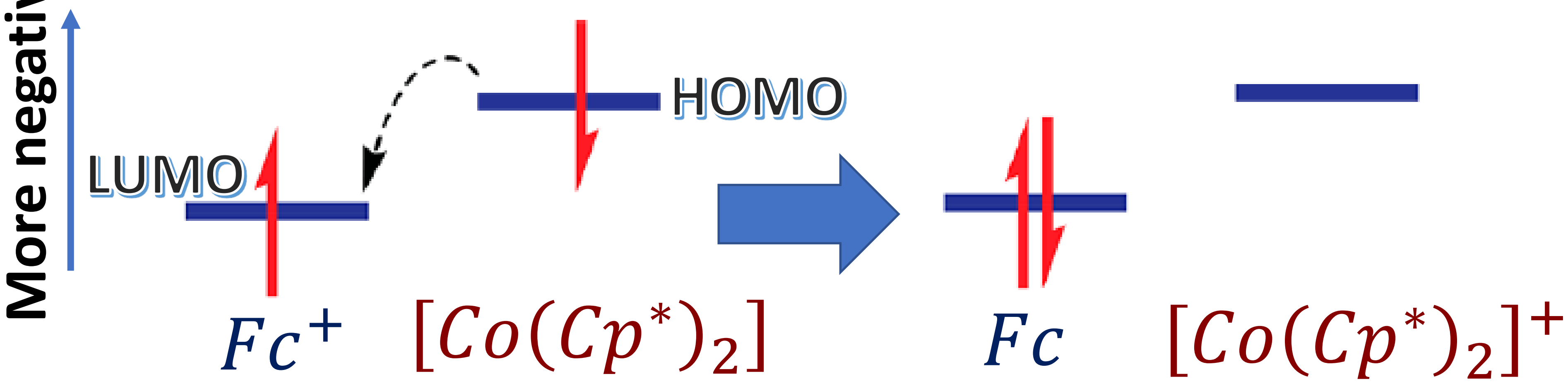
Homogeneous electron transfer using a chemical reductant

Chemical reduction of ferrocenium (Fc^{+} : $[Fe(Cp)_2]^{+}$ (Cp = cyclopentadienyl)) solution to ferrocene (Fc: $[Fe(Cp)_2]$) by $[Co(Cp^{*})_2]$ (Cp* = pentamethylcyclopentadienyl)

$$Fc^{+} + [Co(Cp^{*})_2] \rightleftharpoons Fc + [Co(Cp^{*})_2]^{+}$$

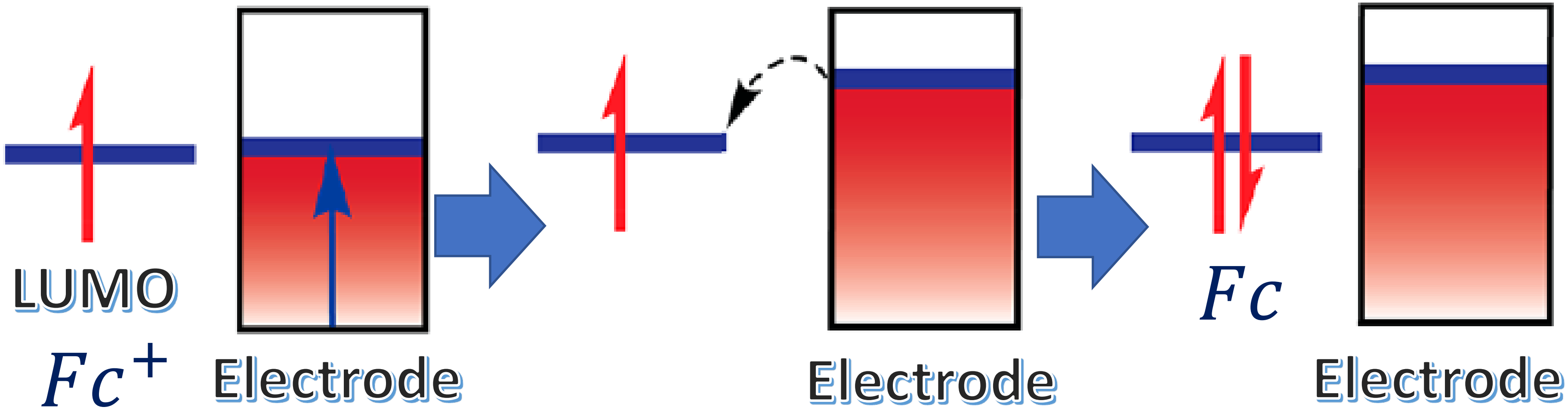


Thermodynamically favorable redn.

Heterogeneous electron transfer at electrode surface

Electrochemical reduction of ferrocenium (Fc$^+$: $[Fe(Cp)_2]^+$ (Cp = cyclopentadienyl)) solution to ferrocene (Fc: $[Fe(Cp)_2]$) at electrode surface

$$Fc^+ + e^- \rightleftharpoons Fc$$



Thermodynamically favorable reduction

Nernst equation; reversible conditions

$$E = E^0 + \frac{RT}{nF} \ln \frac{(Ox)}{(Red)} \qquad E = E^0 + \frac{2.3026\, RT}{nF} \log \frac{(Ox)}{(Red)}$$

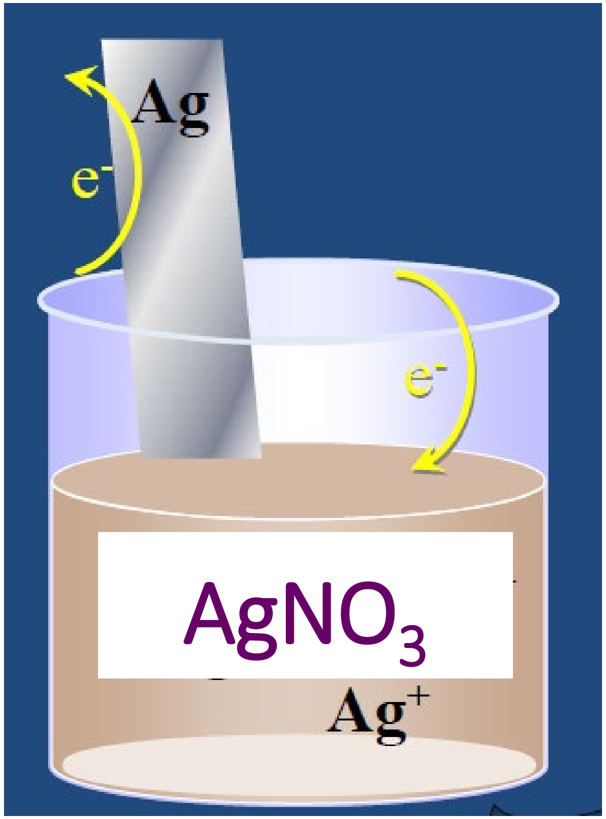
- E: electrode potential,
- E^0: standard electrode potential,
- $\frac{(Ox)}{(Red)}$: relative activities of the oxidized (Ox) and reduced (Red) analyte in the system at equilibrium,
- F: is Faraday's constant,
- R: is the universal gas constant,
- n: is the number of electrons, and
- T: is the temperature

Conditions of reversibility: Single electrode

$$\mathrm{Ag} \xrightarrow{i_+} \mathrm{Ag}^+ + \mathrm{e}^-$$ Anode

$$\mathrm{Ag}^+ + \mathrm{e}^- \xrightarrow{i_-} \mathrm{Ag}$$ Cathode

$$I_{\mathrm{net}} = i_+ - i_-$$



At equilibrium /Reversibility

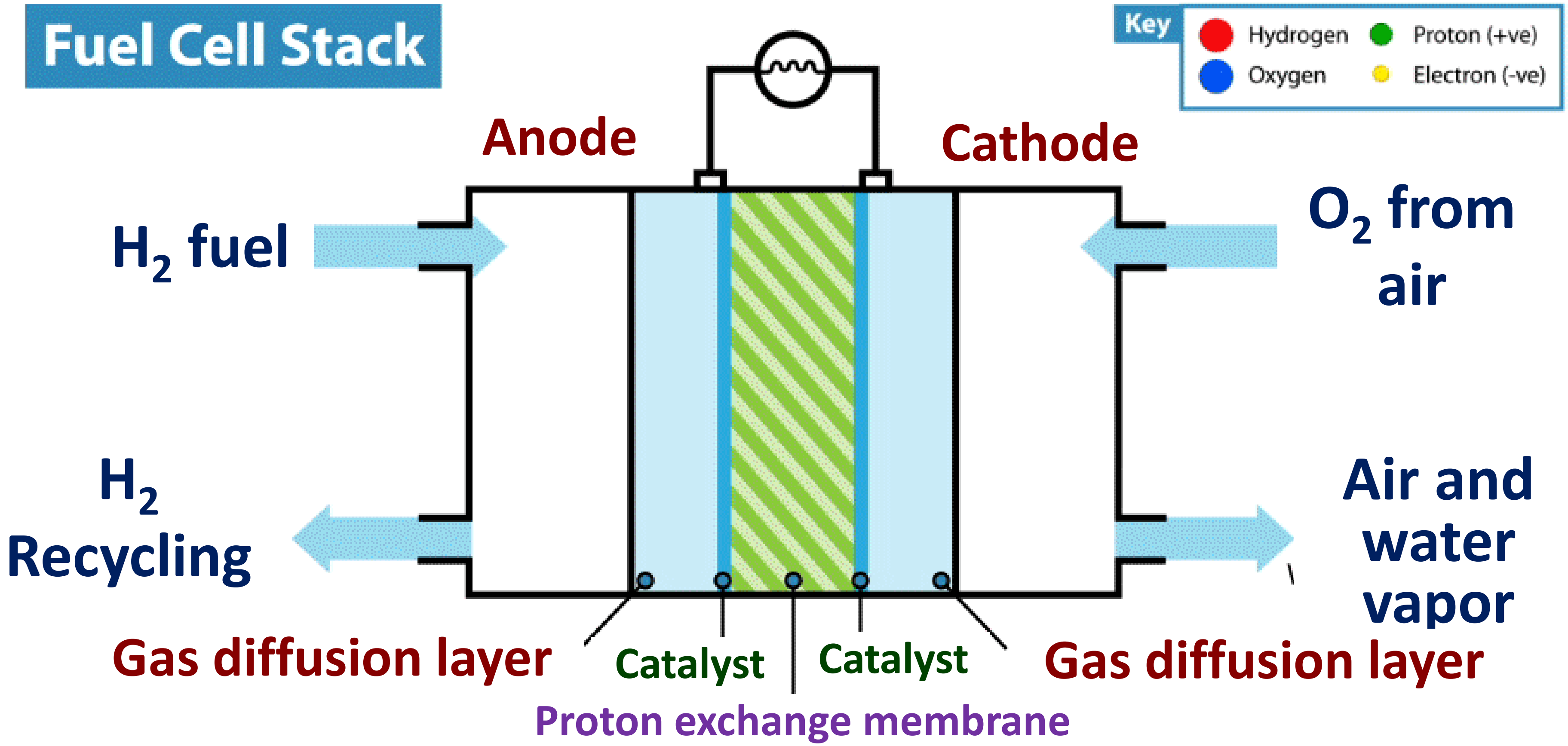
$$\mathrm{Ag}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{Ag}$$

$i_+ = i_-$ $\quad I_{\mathrm{net}} = i_+ - i_- = 0$

The potential (typically measured against a reference electrode) under a condition of reversibility ($I_{net} = 0$) is called the equilibrium ($E_{I=0}$) or reversible (E_{rev}) potential

H_2/O_2 Fuel Cells

Fuel Cell Stack



Key
● Hydrogen ● Proton (+ve)
● Oxygen ● Electron (-ve)

Anode

Cathode

H_2 fuel

O_2 from air

H_2 Recycling

Air and water vapor

Gas diffusion layer

Catalyst

Catalyst

Gas diffusion layer

Proton exchange membrane

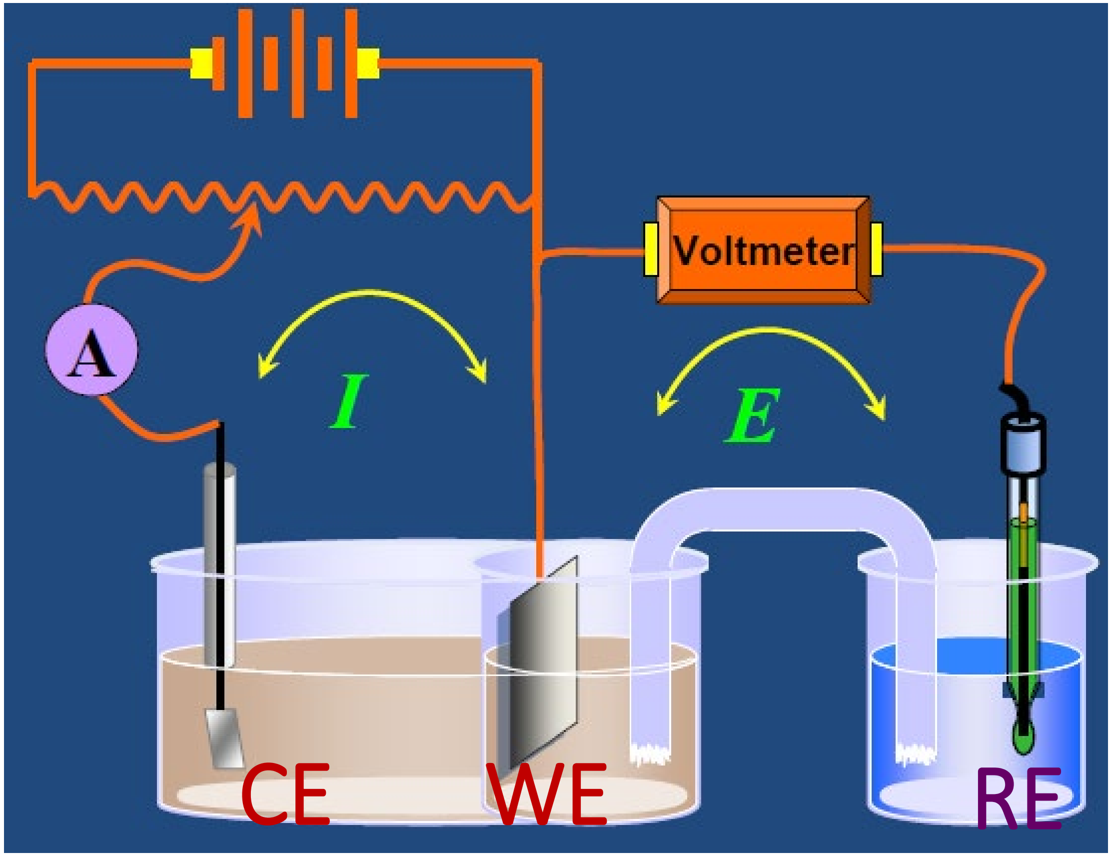
Anode $H_2 \rightarrow 2H^+ + 2e^-$ $E^o = 0 \text{ V}$

Cathode $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^o = 1.229 \text{ V}$

Overall $2H_2(g) + O_2(g) \rightarrow 2H_2O\ (l)$ $E^o = 1.229 \text{ V}$

E_i in three-electrode cells

$$E_i = E_{WE} - E_{RE}$$



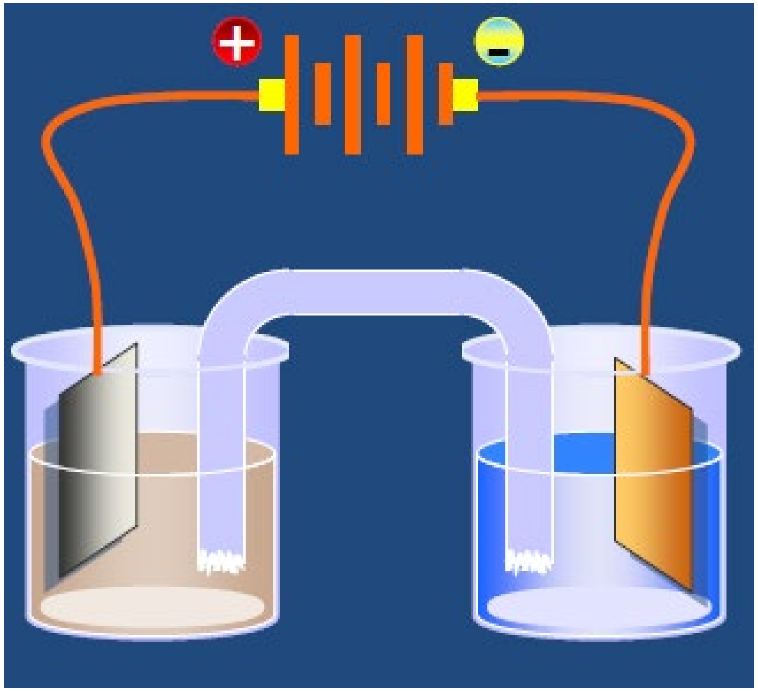
CE: counter (Auxiliary) electrode: completes the circuit to measure the current without impeding its passage, e.g., Pt sheet.

Polarization (p, η): deviation from equilibrium

- Anodic: the electrode is connected to the +Ve pole of an electrical source
- Cathodic: the electrode is connected to the –Ve pole of an electrical source

$i_+ \neq i_-$

Anodically polarized



$$I_{net} = i_+ - i_- \neq 0$$

$$E = E_i = E_{ext}$$

Irreversible

$$p = E_i - E_{rev}$$

$$p = E_i - E_{I=0}$$

Cathodically polarized

Anodic Polarization

$$i_+ \ggg i_-$$

$$\boxed{I_{net} = i_+ - i_- = \text{anodic current}}$$

+ve current

Cathodic Polarization

$$i_+ \lll i_-$$

$$\boxed{I_{net} = i_+ - i_- = \text{cathodic current}}$$

–ve current

Polarization (p)/Overpotential (η)

$E_{I=0}$: is called also the open circuit potential

For a single redox process

$E_{I=0}$: is **equilibrium potential** calculated using Nernst equation

$$p = E_i - E_{rev}$$

$$\eta = E_i - E_{I=0}$$

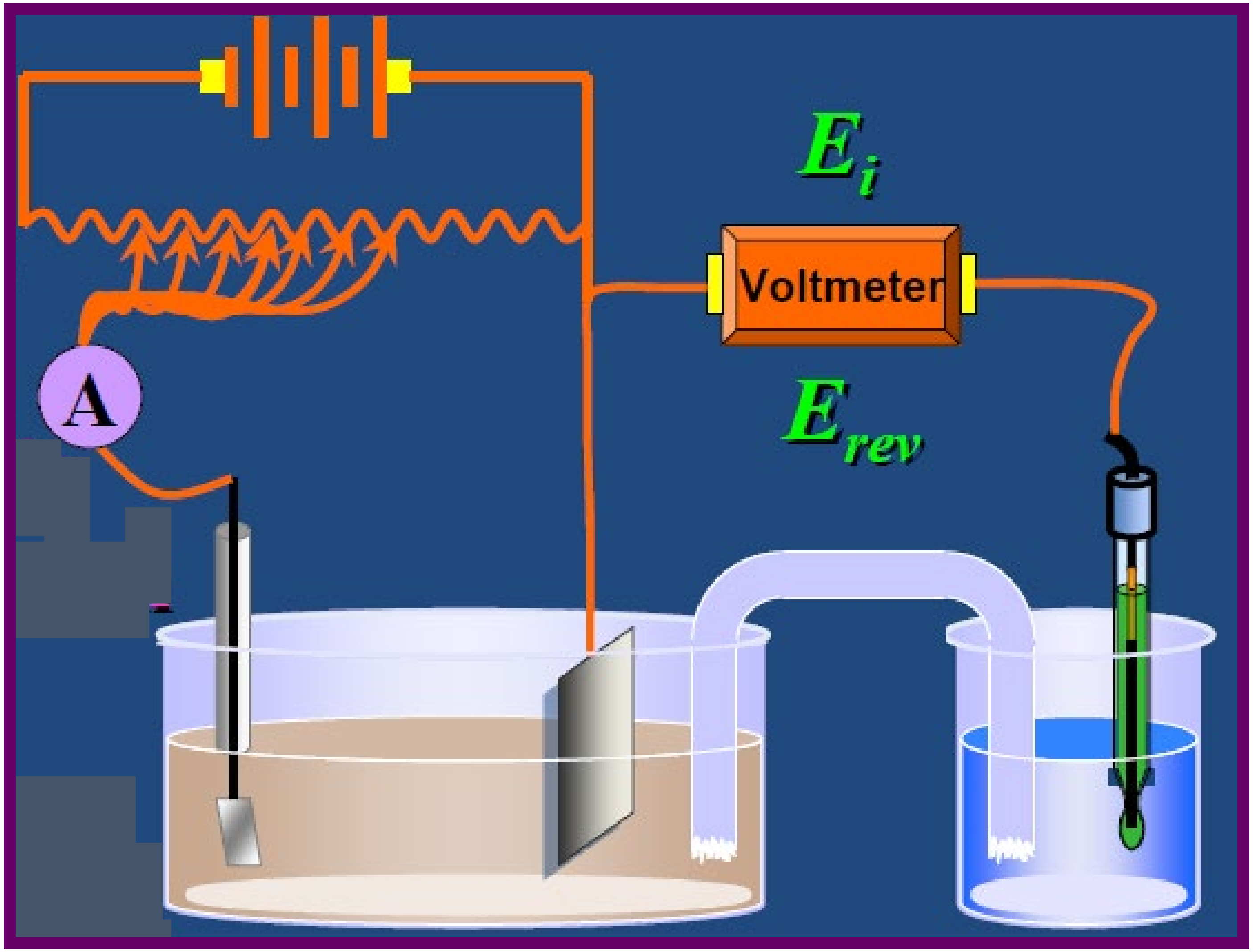
Overpotential or Overvoltage, η

is the extra potential over the equilibrium potential that drives the process in a specific direction at a given rate

Sign convention of η

Anodic polarization, $\eta_a > 0$

Cathodic polarization, $\eta_c < 0$



Rate of electrochemical reaction

Current density (A cm^{-2}):

is a measure for the rate of redox processes running at the anode and cathode of the electrolytic cell.

$$Ox + n\,e^{-} \rightarrow Red$$

$$Rate = -\frac{dN_{ox}}{dt} = \frac{dN_{Red}}{dt}$$

$$mol\,cm^{-2}s^{-1}$$

Inspect the unit

$$\frac{i}{nF} = \frac{Acm^{-2}}{\left(\frac{mol\,e^{-}}{mol\,Ox}\right)\left(\frac{C}{mol\,e^{-}}\right)} = \frac{\frac{C}{s}cm^{-2}}{\left(\frac{C}{mol\,Ox}\right)} = mol\,cm^{-2}s^{-1}$$

Rate of electrochemical reaction

$$Ox + n\,e^{-} \rightarrow Red$$

$$Rate = \frac{i}{nF}$$

Current density (A cm^{-2}):

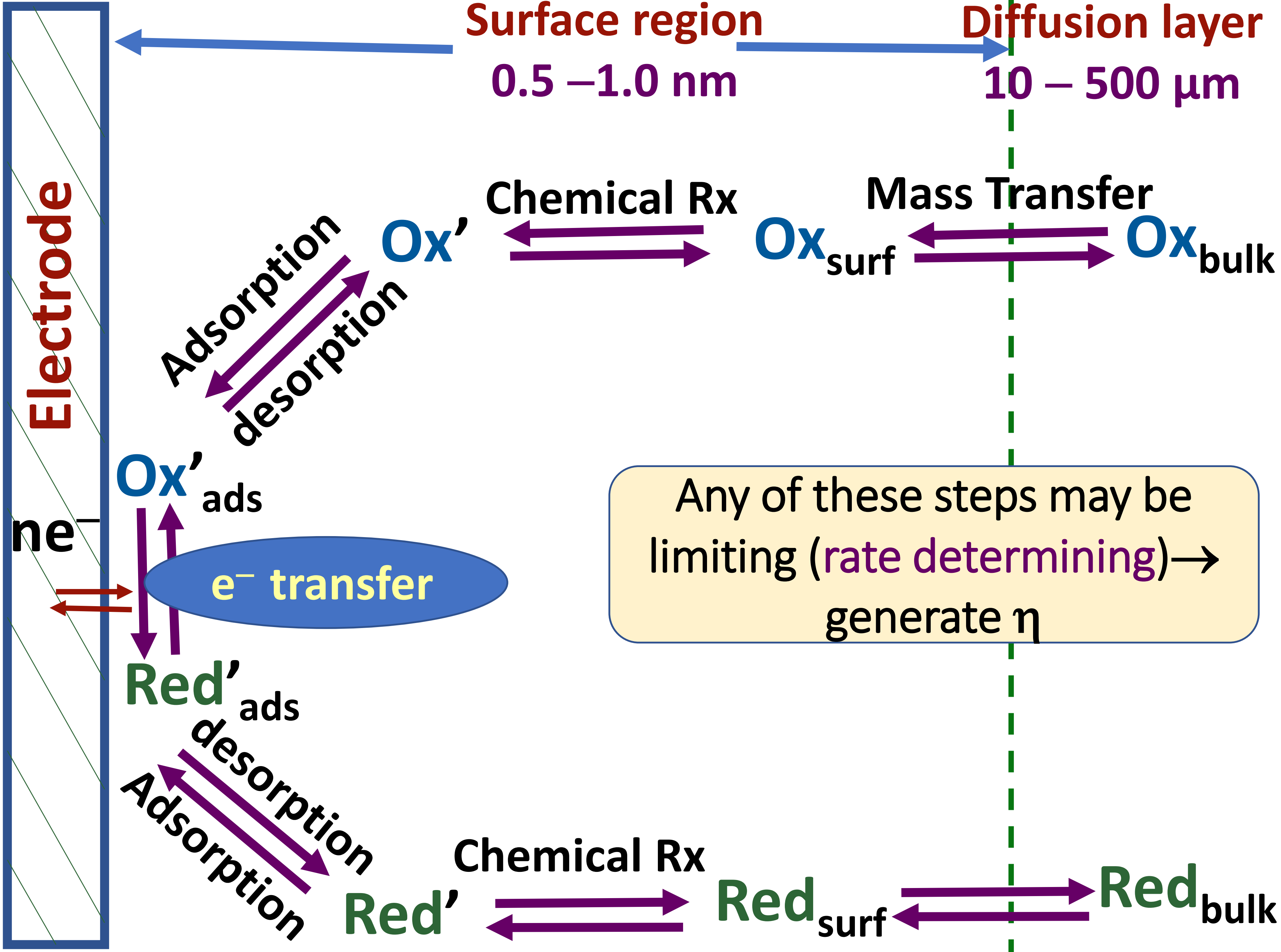
can easily probe the rate of electrochemical reactions.

- As electrochemical reactions concern with the material change and charge transfer at the Electrode/electrolyte interface, equations concern with surface area of the electrode not the volume of the electrolyte in the rate's calculations.

Steps of an electrochemical reaction

$$Ox + n\,e^{-} \rightarrow Red$$

- **Mass transfer** (diffusion, migration, convection) of reactants from the bulk solution to the double layer.
- **Possible chemical reaction** (dissociation of a molecule, dehydration of an ion, structural change, crystallization of a metal or a salt, …etc).
- **Adsorption** of reactants onto the electrode surface.
- **Charge transfer** (Electrode/reactants) across the double layer.
- **Desorption** of the product off the electrode surface.
- **Possible chemical reaction** (hydration of an ion, association of a molecule, …etc).
- **Mass transfer** (diffusion, migration, convection) of Products from electrode surface to the bulk solution.



Surface region

0.5 –1.0 nm

Diffusion layer

10 – 500 µm

Electrode

Chemical Rx

Mass Transfer

Ox' ⇄ Ox_{surf} ⇄ Ox_{bulk}

Adsorption

desorption

Ox'_{ads}

ne^-

e⁻ transfer

Red'_{ads}

desorption

Adsorption

Chemical Rx

Red' ⇄ Red_{surf} ⇄ Red_{bulk}

Any of these steps may be limiting (rate determining)→ generate η

Concentration Polarization (η_c)

- results when the concentrations of reactants/products at the electrode surface are different under non-equilibrium conditions from their values under equilibrium (bulk) values.

- grows and decays slowly on application and interruption of current at a rate characteristic of the diffusion coefficients of the species involved.

- is the only form of η affected by stirring and is unaffected by the nature of electrode surface.

Activation Polarization (η_a)

- is also called **charge transfer** polarization, η_{ct}

- is the polarization needed to promote the ECR in one direction and retard it in the opposite direction.

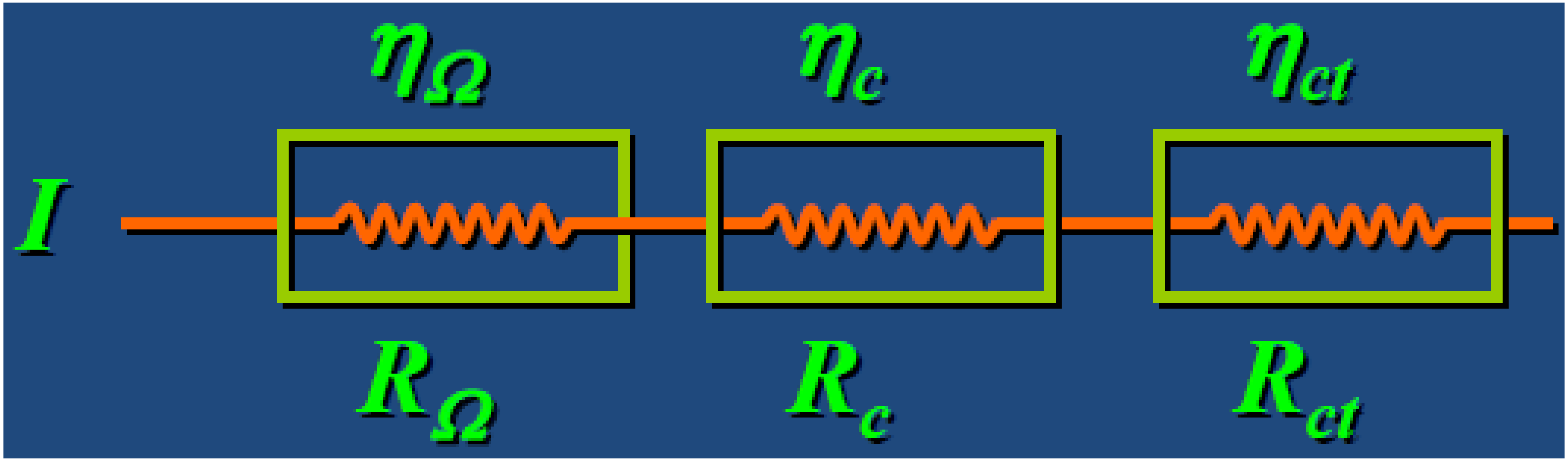
- appears as a change in the value of potential difference across the electrical double layer between non-equilibrium and equilibrium.

Ohmic (Resistance) polarization, η_Ω

- results from the current flow in resistive electrolytes (R_{sol}), and/or electrodes (R_{e}: oxide films or salts, gas bubbles, grease, dirt, ..etc). **Heating effect**.
- Even with using electrodes of very low resistance and with using electrolytes of very high ionic conductivity and with using Luggin capillary, there remains a sort of uncompensated (unaviodable) resistance, R_{u}.
- It appears and disappears instantaneously when the polarizing current is imposed or disconnected

$$\eta_{\Omega} = I \times R = I \times (R_{\mathrm{e}} + R_{\mathrm{sol}} + R_{\mathrm{u}})$$

Generally,



$$\eta = \eta_\Omega + \eta_c + \eta_{ct}$$

The degree of reversibility in a given ECR depends on the rates of mass and charges transfers involved

Reversible **Quasi-reversible** **Irreversible**

Reversible processes

Rate of charge transfer >>> Rate of mass transfer

Mass transfer controlled

- stays close to equilibrium (Nernst equation applies) regardless of the passing current.
- $\eta_{ct} = 0$.
- in absence of η_{Ω} , $\eta = \eta_c$

Quasi-reversible processes

Rate of charge transfer <<< Rate of mass transfer

Charge transfer controlled

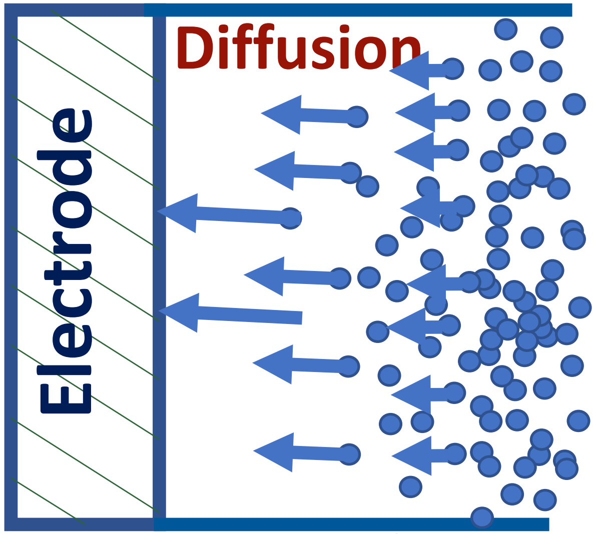
- $\eta_c = 0$.
- In absence of η_Ω , $\eta = \eta_{ct}$

Irreversible processes

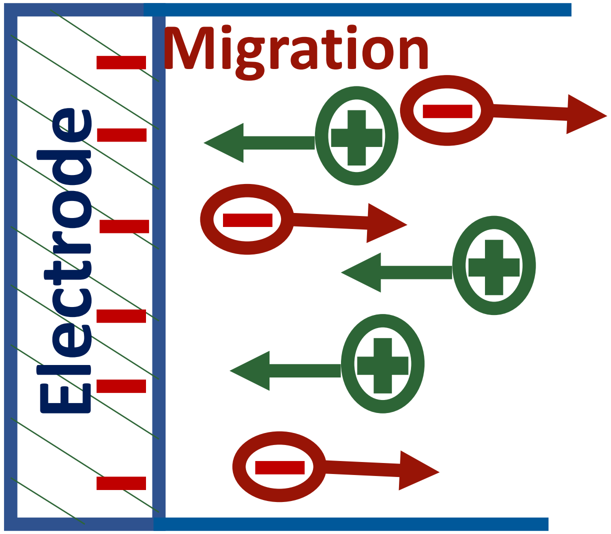
Rates of charge and mass transfers are comparable

- In absence of η_Ω , $\eta = \eta_c + \eta_{ct}$

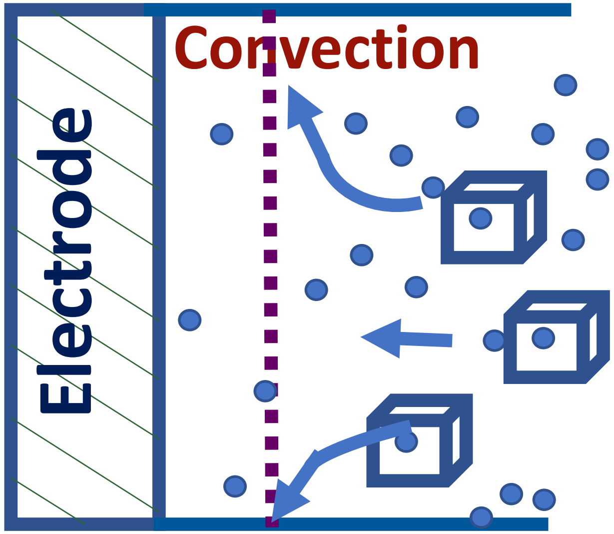
Concentration (mass transport) overpotential, η_c



Concentration gradient



Electric potential gradient



Pressure gradient

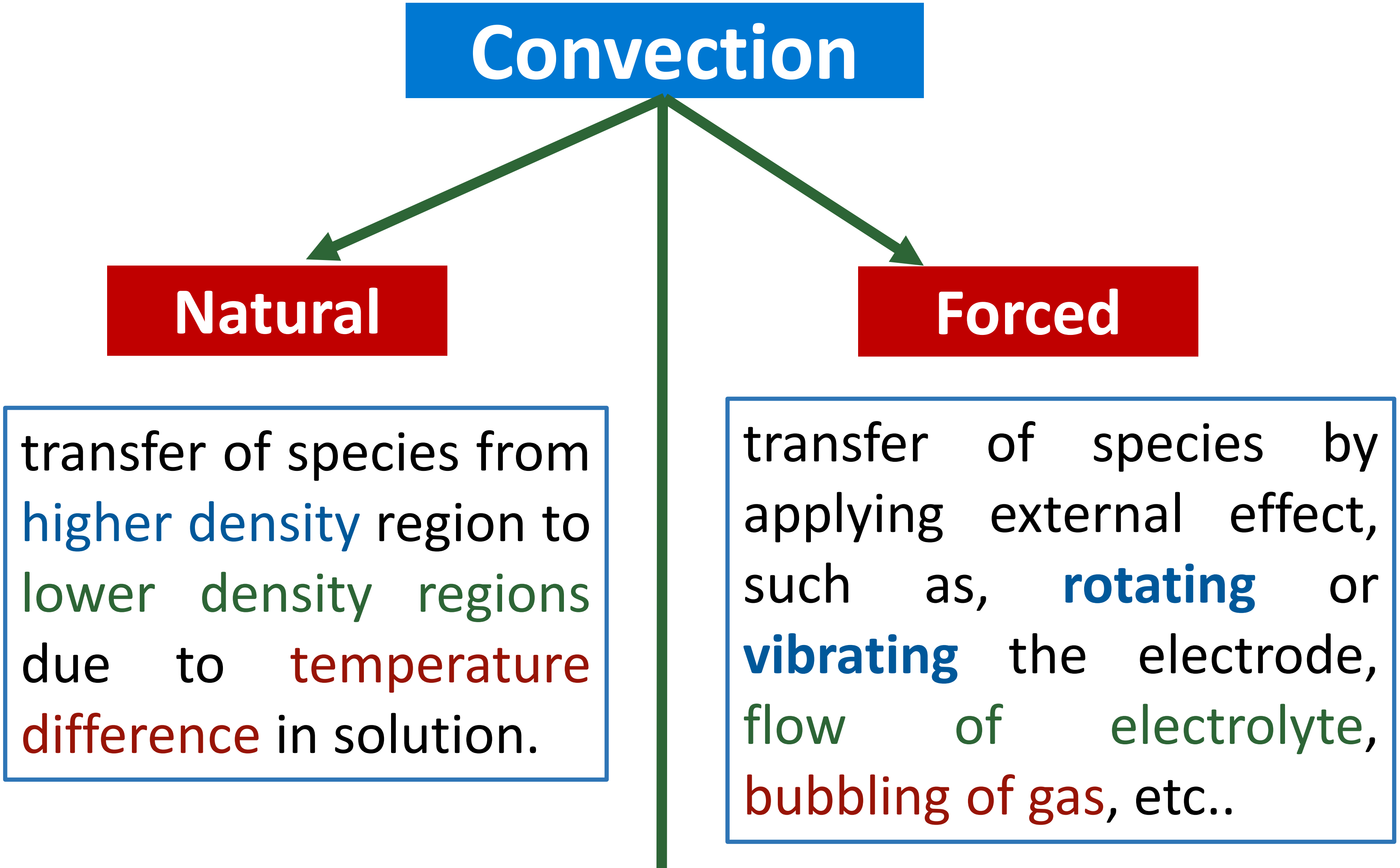
Migration

- transfer of ions under the effect of electric field (Potential difference between anode and cathode in the cell).

- all ions contribute in carrying current according to their concentration, charges and transport numbers.

Convection

- transfer of ions under a pressure difference



Convection

Natural

Forced

transfer of species from higher density region to lower density regions due to temperature difference in solution.

transfer of species by applying external effect, such as, **rotating** or **vibrating** the electrode, flow of electrolyte, bubbling of gas, etc..

Diffusion

- Mass transfer due to a concentration difference.

- The direction of diffusion is from the region of high concentration to the region of lower concentration.

- In diffusion and convection, only redox species under study contribute to current

Concentration overpotential

- The electrical energy ($nF\eta_c$) needed to speed up the mass transfer.
- Fast chemical reactions that precede or follow the charge transfer affect the concentration of redox species and hence, contribute to η_c

In absence of convection

$$I_{\mathrm{mt}} = I_{\mathrm{m}} + I_{\mathrm{d}}$$

Mass transfer current

Migration current

Diffusion current

Calculation of Concentration overpotential

1- *Diffusion and migration considered:*

Consider this reversible process

$$Ox + ne^{-} \rightleftharpoons Red$$

The mathematical equation depends on

- State Ox and Red (soluble or insoluble)
- The initial presence or absence of either Ox or Red.
- Shape of electrode.
- Convection.

To make the derivation possible we need to set few assumptions

Assumptions

Reversible: fast charge transfer

$$\mathbf{Ox} + \mathbf{ne^-} \rightleftharpoons \mathbf{Red}$$

1) Ox undergoes reduction by cathodic polarization.
2) The cathode electrode is planar.
3) Solution is so large around the electrode that a semi-infinite linear diffusion occurs.
4) Ox (metal ion) is initially present and Red (metal) is initially absent. Activity of Red is constant and taken as unity.
5) Solution and electrode are stagnant (no convection).

At a current density, i: $\eta_c = E_i - E_{rev}$

Since the process stays at equilibrium at any i, Nernst equation may apply to calculate E_i but assuming a surface concentration for Ox of $C_{e(ox)}$

$$E_i = E^0 + \frac{RT}{nF} \ln C_{e(Ox)}$$

Irreversible

Before electrolysis, equilibrium (reversible conditions) is assumed, and the surface concentration $C_{e(Ox)}$ equals the bulk concentration $C_{0(Ox)}$

$$E_{rev} = E^0 + \frac{RT}{nF} \ln C_{0(Ox)}$$

Reversible

$$\eta_c = E_i - E_{rev} = \frac{RT}{nF} \ln \frac{C_{e(Ox)}}{C_{0(Ox)}}$$

$C_{e(Ox)}$ is not a directly accessible quantity

Determination of $\frac{C_{e(Ox)}}{C_{0(Ox)}}$

- $C_{e(Ox)}$ reaches the electrode surface by migration and diffusion.

$$I_m = t_{Ox} \times i$$

where t_{ox} is the transport number (fraction of current carried by Ox) of Ox

I_d is obtained from Fick's first law of diffusion

Fick’s first law of diffusion

$$J = -D\frac{\partial C}{\partial x}$$

- It relates the diffusive flux to the concentration under the assumption of steady state (state variables are unchanged with time).
- It postulates that the flux (J) goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient.

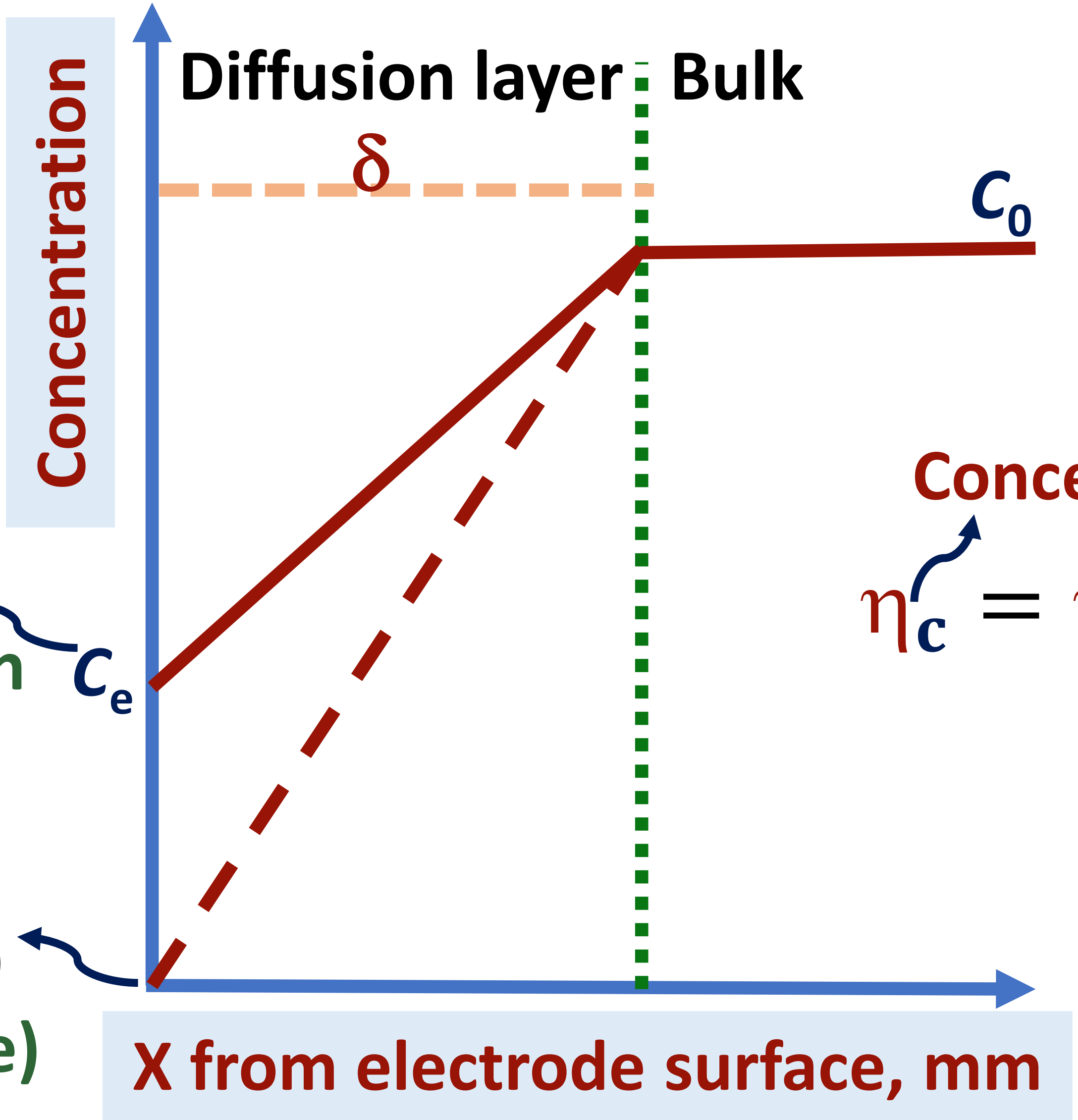
J (diffusion flux): measures the amount of substance that will flow through a unit area during a unit time interval.

$$J:\ mol\,m^{-2}s^{-1}$$

- $\boldsymbol{D}\ (\boldsymbol{m^{2}s^{-1}})$: diffusivity or diffusion coefficient
- $\boldsymbol{C}\ (\boldsymbol{mol\ m^{-3}})$: Concentration.
- $\boldsymbol{x}\ (\boldsymbol{m})$: distance from electrode surface

Assumption

The surface concentration of active species ($C_{e(Ox)}$) is changed linearly within the diffusion layer of thickness δ (≈ **10 – 500 μm**).



Surface concentration C_e

$C_e=0$ **when**

$\eta_c \rightarrow \infty$ (√)

$\eta_d \rightarrow \infty$ (note)

Concentration

$$\eta_c = \eta_m + \eta_d$$

Migration

Diffusion

With this assumption

$$J = -D\frac{\partial C}{\partial x} = -D\frac{\left(C_{0(Ox)} - C_{e(Ox)}\right)}{\delta}$$

J represents the rate of transferring Ox species to the surface.

$$Ox + n\,e^{-} \rightarrow Red$$

$$Rate = J = -\left(\frac{dN_{Ox}}{dt}\right)_{x=0} = \frac{-i_d}{nF} \qquad mol\, m^{-2} s^{-1}$$

The negative sign was added to infer the decrease of N_{Ox}

$$D\frac{\left(C_{0(Ox)}-C_{e(Ox)}\right)}{\delta}=\frac{i_d}{nF}$$

$$\boxed{i_d=\frac{nFD\left(C_{0(Ox)}-C_{e(Ox)}\right)}{\delta}}$$

For simplicity, let

$$k=\frac{nFD}{\delta}$$

$$i_d=k\left(C_{0(Ox)}-C_{e(Ox)}\right)$$

Coming back to I_{mt}

The process is assumed reversible, i.e., the process is mass transfer limited and the overall rate (*i*) is controlled by the mass transfer current (I_{mt})

$$\begin{tikzcd} & I_{mt} = i = I_m + I_d \arrow[dl, bend right] \arrow[dr, bend left] & \\ I_m = t_{Ox} \times i & & i_d = k\left(C_{0(Ox)} - C_{e(Ox)} \right) \end{tikzcd}$$

$$i = \left(t_{Ox} \times i\right) + \left(k\left(C_{0(Ox)} - C_{e(Ox)} \right)\right)$$

$$i - \left(t_{Ox} \times i\right) = k\left(C_{0(Ox)} - C_{e(Ox)} \right)$$

$$i\left(1 - t_{Ox}\right) = k\left(C_{0(Ox)} - C_{e(Ox)} \right)$$

$$i = \frac{k\left(C_{0(Ox)} - C_{e(Ox)} \right)}{\left(1 - t_{Ox}\right)}$$

Limiting conditions: when $\eta_c \rightarrow \infty$, $C_{e(Ox)} \rightarrow 0$

- ○ It means when E_{irr} is too high, the maximum flow of Ox to the surface is insured and the maximum current (is supposed limiting), i_L, is as well obtained.

- ○ Note that we are assuming from at the beginning that the charge transfer is fast, hence, Ox will be reduced as soon as it reaches the surface to make $C_{e(Ox)} \approx 0$

$$i_{\eta\rightarrow\infty} = i_L = \frac{k\,C_{0(Ox)}}{(1 - t_{Ox})}$$

$$k = \frac{nFD}{\delta}$$

Maximum mass transfer current or (limiting) current density

$$i_{\eta\to\infty} = i_L = \frac{k\, C_{0(Ox)}}{(1 - t_{Ox})}$$

- i_L is directly proportional to $C_{0(Ox)}$ if k and $(1 - t_{Ox})$ were constants; which is useful for analysis.

- In fact, while k is independent of $C_{0(Ox)}$, $(1 - t_{Ox})$ which represents the migration contribution of all ions in the solution except Ox depends on $C_{0(Ox)}$.

Calculation of Concentration overpotential

2- Diffusion only considered:

$$\mathrm{Ox} + \mathrm{ne}^{-} \rightleftharpoons \mathrm{Red}$$

How to minimize i_m and η_m.

1) The same previous assumptions are still applied.
2) The charge transfer is still assumed fast.
3) A supporting electrolyte (as KCl: inert ionic species that undergoes neither oxidation nor reduction) is added in a large excess amount. Hence, most of i_m will be carried by inactive species.

$$(1 - t_{Ox}) \approx 1$$

4) The overall passing current will be totally diffusional.

$$i = i_d \qquad \eta_c = \eta_d$$

$$i_d = k\left(C_{0(Ox)} - C_{e(Ox)} \right)$$

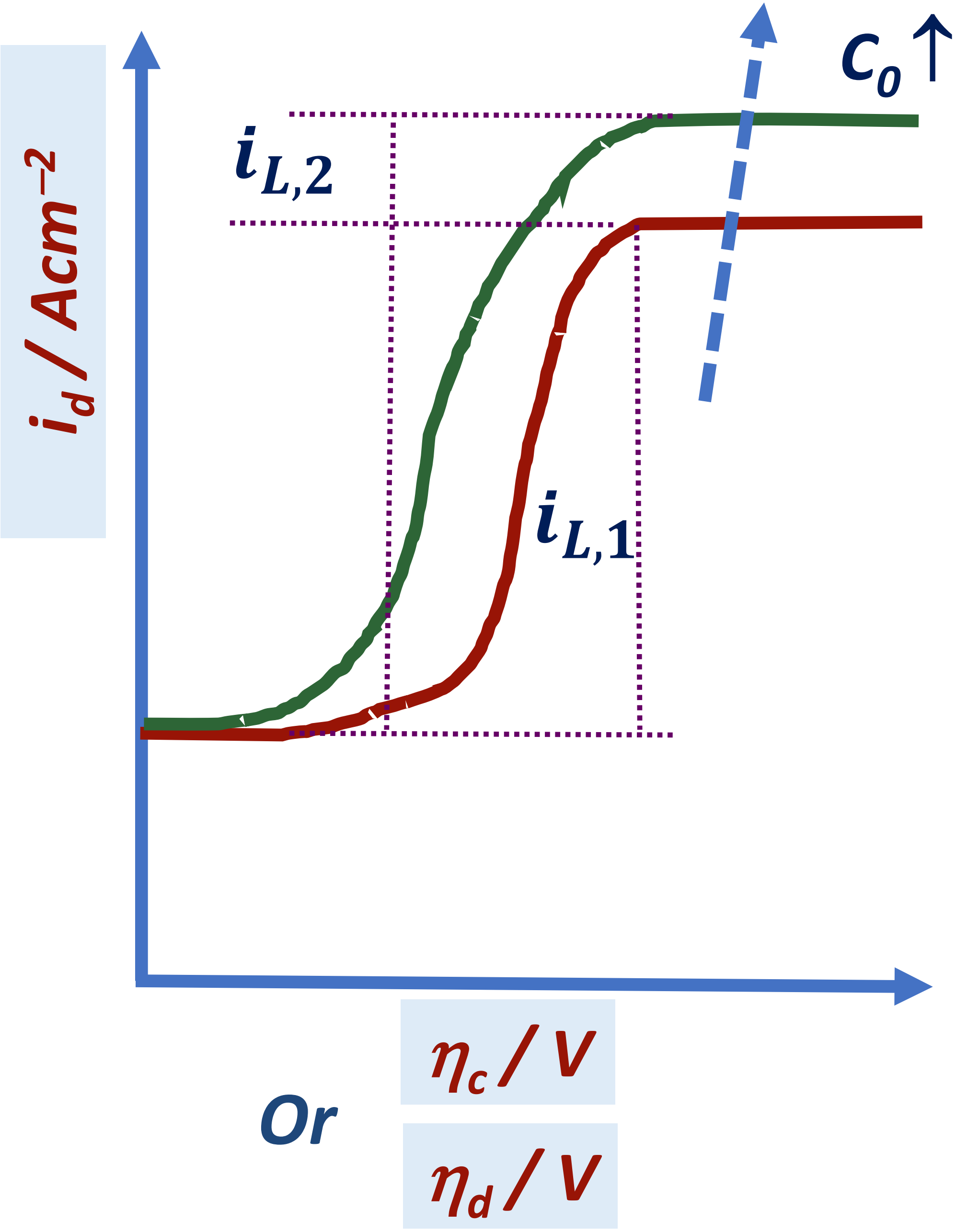
$$i_L = k\, C_{0(Ox)}$$

$$\Rightarrow \quad \frac{i_d}{i_L} = \frac{\left(C_{0(Ox)} - C_{e(Ox)} \right)}{C_{0(Ox)}}$$

$$\Rightarrow \quad \boxed{\frac{C_{e(Ox)}}{C_{0(Ox)}} = \left(1 - \frac{i_d}{i_L} \right)}$$

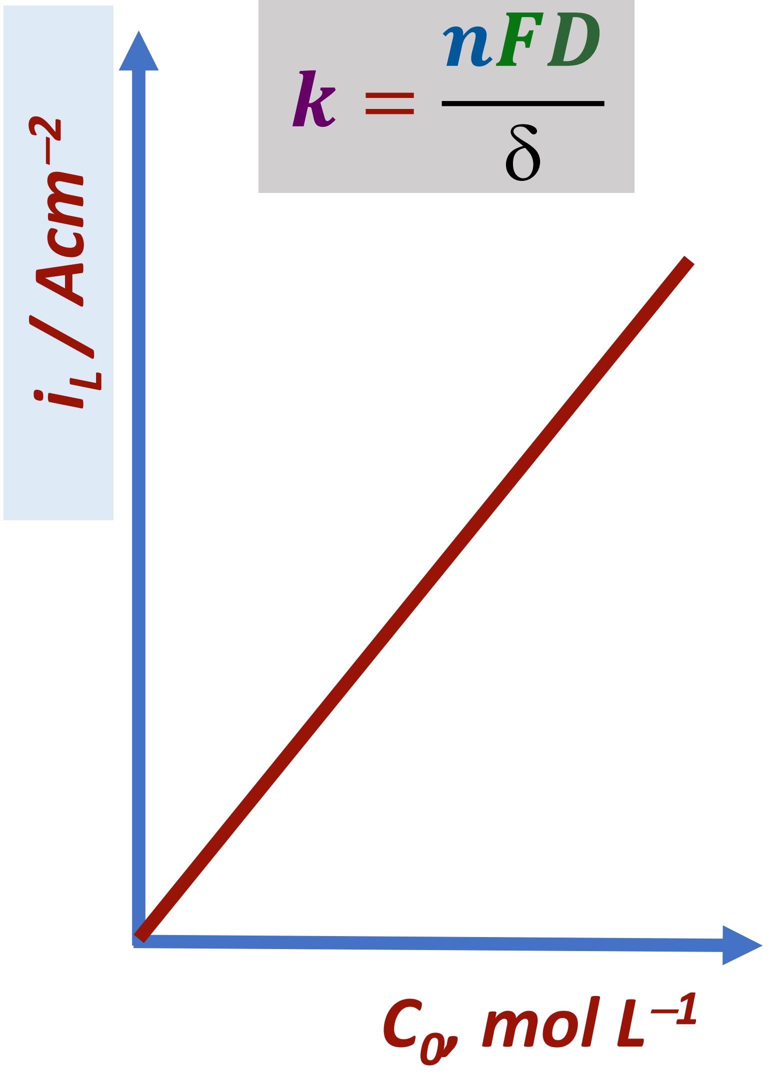
- Since i_d and i_L can be measured experimentally, η_c can be estimated:

$$\eta_c = E_i - E_{rev} = \frac{RT}{nF} \ln \frac{C_{e(Ox)}}{C_{0(Ox)}} = \frac{RT}{nF} \ln \left(1 - \frac{i_d}{i_L} \right)$$



$$i_{\eta\to\infty} = i_L = k\,C_{0(Ox)}$$

$$k = \frac{nFD}{\delta}$$



Minimizing η_c

$$\eta_c = E_i - E_{rev} = \frac{RT}{nF} \ln \frac{C_{e(Ox)}}{C_{0(Ox)}} = \frac{RT}{nF} \ln\left(1 - \frac{i_d}{i_L}\right)$$

- ○ We are considering cathodic polarization; when η_c increases in negativity, the power consumption increases which is not desirable.
- ○ i_d can never be zero as we are addressing a diffusion controlled process and will not exceed i_L.
- ○ Hence, $0 < \frac{i_\mathrm{d}}{i_\mathrm{L}} < 1$. To maintain η_c minimum or closer to zero, i_d has to be much smaller than i_L so that:

$$\frac{i_d}{i_L} \approx 0$$

- ○ Using very low i_d compared to i_L.
- ○ Using high Ox concentration (i.e., high i_L)

Calculation of Diffusion coefficient, D

- The diffusion layer thickness, δ depends on D

$$\delta = \sqrt{Dt}$$

t is the time of polarization

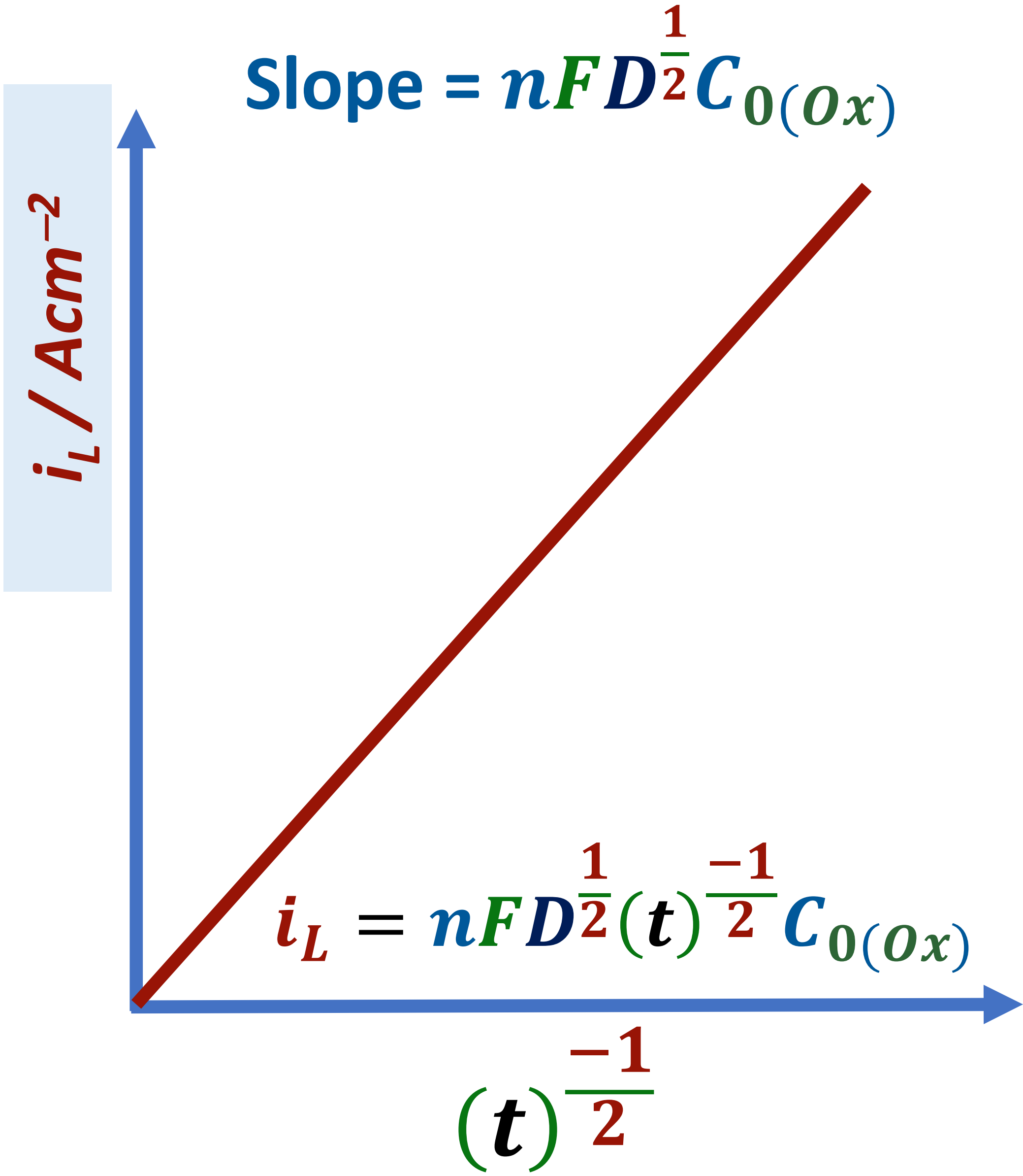
$$\boxed{i_d = \frac{nFD\left(C_{0(Ox)} - C_{e(Ox)}\right)}{\delta}}$$

$$i_L = \frac{nFD\,C_{0(Ox)}}{\delta} = \frac{nFD\,C_{0(Ox)}}{\sqrt{Dt}}$$

$$= \frac{nF\sqrt{D}\,C_{0(Ox)}}{\sqrt{t}} = nFD^{\frac{1}{2}}(t)^{\frac{-1}{2}}C_{0(Ox)}$$

In a relaxation experiment:

- E vs. t at constant I or I vs. t at constant E are measured. Then E vs. I curves are automatically created.
- A sufficient high potential is applied to reach i_L region and i_L is plotted against $(t)^{\frac{-1}{2}}$ to calculate the fundamental mass transfer parameter (D) from the slope.



Slope = $nFD^{\frac{1}{2}}C_{0(Ox)}$

$$i_L = nFD^{\frac{1}{2}}(t)^{\frac{-1}{2}}C_{0(Ox)}$$